OPTICAL ACTIVITY AND POLARITY OF SUBSTITUENT GROUPS AS EXHIBITED IN MENTHYL ESTERS.

by

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Thesis for the Degree of Ph.D.

C O N T E N T S.

A connection between optical activity and chemical constitution was first demonstrated in 1874, when van't Hoff and Le Bel independently developed the theory that optical activity was due to asymmetry of molecular structure.

Sixteen years later, Guye[1] suggested that rotatory power was dependent on the weight of the four groups attached to the asymmetric carbon atom, and on the distances of their respective centres of gravity from this atom. On this view the optical activity of a compound should be zero when two of the groups are equal in weight, and similarly disposed about the asymmetric atom. It was shown, however, by Walden[2] that compounds of this type often possessed a high rotatory power. For these and other reasons Guye's hypothesis has been abandoned.

About the same time Crum Brown[3] proposed to calculate the asymmetry of the molecule by attaching a value K to each radical linked to the asymmetric atom. This value was stated to be a function of the composition and constitution of the radical, and not necessarily proportional to the mass or to the distance/

1 Comptes rendus de l'Academie des sciences, 1890, 110, 714; 1893, 116, 1378.
2 Zeitschrift fur Physikalische Chemie 1895, 17, 245.
3 Proceedings of the Royal Society of Edin. 1890, 181.

distance of the centre of gravity from the centre of the tetrahedron. Unfortunately it has not been possible to test this theory, because no means of assigning a definite physical significance to the value K has yet been suggested.

Over thirty years have elapsed since the above theories were put forward, and yet very little progress has been made towards establishing regularities between chemical constitution and the magnitude of rotatory power.

In general it is found that the presence of unsaturated groups increases the rotatory power of a compound, although many exceptions to this rule are known[1]. Similarly the rotation of a compound is related to ionisation (Oudemann's Law), and Hudson[2] succeeded in showing that, in acids of the sugar group containing α-, β-, γ-, and δ- asymmetric carbon atoms, the rotation in aqueous solution due to the α- carbon atom was very much larger than the values due to the other three carbon atoms added together, and thus the direction of rotation of the phenylhydrazide could be used as an indication of the configuration of the hydroxyl group attached to the α- atom.

It/

1 Hilditch, Journal of the Chemical Society, 1908, 93, 701; 1911, 99, 218.
Pickard and Kenyon, J.C.S., 1911, 99, 46.

2 Journal of the American Chemical Society, 1917, 39, 462.

It has recently been shown by Betti, in papers summarised in Gazzetta Chimica Italiana, 1923, 53, 417, that in certain compounds examined by him a definite parallel could be drawn between the influence of substituents on optical activity and on acidity. Betti prepared a large number of condensation products of an active base with substituted benzaldehydes (thirty-six in all) and found that the influence of substituents in the benzene nucleus agreed very closely with their influence on the acidic strength of the corresponding benzoic acids. If the rotations of these compounds are analysed it is found that the groups can be arranged thus:-

ortho- groups:- $NO_2 > CH_3 > Cl > OH > H > OCH_3$

para- " :- $NO_2 > Cl > H > CH_3 > OH > OCH_3 > (N\ Me_2)$

The influence of the o-substituents on acidity is given by $NO_2 > Cl > OH > CH_3 > OCH_3 > H > N\ Me_2$

The agreement of both ortho and para series with acidity is broken only by displacement of the hydrogen and methyl compounds.

It has also been observed by Rule* that the influence of substituents on the rotation of certain amyl derivatives and of menthyl esters of ortho-substituted/

* J.C.S., 1924, 125, 1126.

substituted benzoic acids corresponds very closely with their influence on the nitration of mono-substituted benzenes. In this case the influence of the groups is represented by the sequence

$$CH_3O,\ F,\ Cl,\ Br,\ [CH_3,\ I,]\ H,\ COOH,\ NO_2.$$

Here the unsaturated groups, all of which, like hydrogen, are positive according to Lapworth's principle[1] raise the rotation; the remaining groups, on the other hand, which are described by him as negative, depress the rotation. In addition it has been pointed out by Rule[2] that the above series closely represents the true relative polarity of the groups, as deduced from the views of J.J. Thomson[3].

The term polarity, however, is also used in another sense in the phrase "general polarity"[4]. As so used, the term may be taken to mean the relative influence of simple substituents on acidity, e.g. of acetic acid, thus leading to the series

$$NO_2,\ CN,\ OH,\ Cl,\ Br,\ I,\ OCH_3,\ H,\ CH_3.$$

This "general polar series" can also be traced in the influence of substituents on the dielectric constants of/

1 J.C.S., 1922, 121, 461.

2 loc. cit.

3 Phil. Mag. 1923, (VI), 46, 497.

4 Robinson (Ann. Rep. 1922, 98).

of monosubstituted methanes, ethanes, and benzenes[1], and on the chemical reactivity of benzene derivatives,[2] Later, the latter investigator[3] examined the hydrolysis of substituted benzyl chlorides, and found the velocity constants to be in the order

$$CH_3 > H > \text{Halogens} > COOH > NO_2;$$

this again being in agreement with the general polar series. As has been shown by Rule and Paterson[4], in connection with the reactivity of substituted benzoic anhydrides, the methoxy group falls into the expected position in the neighbourhood of hydrogen.

The investigations of Betti quoted above would point to the existence of a similar general polar effect in optical activity, although, in this case the rotations were only measured at one dilution, in one solvent (benzene), and for light of one wave-length. As is well known, solvents frequently exert a marked influence on rotation, and although Pickard and Keynon[5] have shown that the molecular rotations of certain menthyl esters of substituted benzoic acids are very little altered by the presence of solvents, yet/

1 Rule. (loc. cit.).

2 S.C.J. Olivier. Recueil des travaux chimiques des Pays-Bas, 1914, 33, 244.

3 ibid., 1923, 42, 516, 775.

4 J.C.S. 1924, 125, 2155.

5 J.C.S. 1915, 107, 52.

yet conclusions drawn from measurements at one dilution and in one solvent are always open to criticism. For this reason it is unfortunate that these two investigators were unable to make a complete examination of the optical dispersive character of all of the menthyl esters of ortho substituted benzoic acids prepared by Cohen[1]. The only compounds investigated by these authors were the o-nitro and the o-iodo derivatives in the homogeneous state, and the o-carboxy, o-propoxy, o-iodo, and o-nitro derivatives in solution. It was stated that complex dispersion is shown by the nitro- and carboxy- compounds in certain solutions, but the homogeneous esters exhibited simple dispersion, except the nitro-compound at high temperatures.

A few of the menthyl esters of substituted acetic acids have been examined in the liquid state by Tschugaev[2] (acetate, propionate, butyrate), and Hilditch[3] (brom- acetate, chlor-acetate), but the results are only recorded for light of one wave-length, and at one temperature. At the suggestion of Dr Rule I undertook the preparation of five menthyl esters of substituted acetic acids and of a substituted benzoic acid for the purpose of determining the molecular rotations at four different temperatures, and for lights of four different wave-lengths.

1 J.C.S. 1914, 105, [redacted], 1893.
2 Journal of the Russian Physical Chemical Society, 1902, 34, 606.
3 Journal of the Chemical Society, 1912, 101, 202.

EXPERIMENTAL.

The l-menthol used for the preparation of the following six esters was specially purified material obtained from "The British Drug Houses Ltd"., and had a rotation of $[\alpha]_D^{18}$ = - 49.50 in 5 per cent ethyl alcoholic solution.

Optical measurements were made using a "Schmidt and Haensch" polarimeter capable of holding a two decimetre observation tube. This instrument was specially fitted by A. Hilger, Ltd. with a direct vision spectroscopic attachment for reading rotations with the three mercury lines (yellow, green, and violet).

A considerable amount of trouble was experienced in devising an arrangement whereby a continuous flow of water at constant temperature could be made to pass through the jacket of the observation tube. The most successful results were obtained by making use of the following arrangement:- Water, from a constant head, was slowly passed down the inner tube of a copper condenser into a thermostat, then through the polarimeter tube and finally back through the outer condenser jacket to waste.

Mercury/

Mercury Lamp:- A Cooper Hewitt Silica Lamp for direct current circuits was used as the source of mercury light. All outside tubes were lagged, and in this way the temperature inside the tube could be maintained within $.1^{\circ}$ over a set of readings.

PREPARATION OF MENTHYL ETHOXYACETATE.

This ester was prepared from monochloracetic acid in three stages as follows:-

(1) $Cl.CH_2.COOH \xrightarrow{EtO\ Na} EtO.CH_2.COOH$

(2) $EtO.CH_2.COOH \xrightarrow{SOCl_2} EtO.CH_2.COCl$

(3) $EtO.CH_2.COCl \xrightarrow{Menthol} EtO.CH_2.COOC_{10}H_{19}$

(1) Ethoxyacetic Acid.

This compound was prepared by the method described by Sommelet in * Bull. Soc. Chim., 1907 (IV), 366, as follows:-

69 grammes of sodium were dissolved in 1000 gms. of absolute alcohol contained in a round flask fitted with a reflux condenser; then, without allowing the liquid to cool, a solution of 142 gms. of monochloracetic/

* Bulletin de la Societé chimique de France.

monochloracetic acid in its own weight of absolute alcohol was gradually added. At each addition an energetic action took place with deposition of sodium chloride. As the acid was added fairly quickly the boiling of the liquid was not interrupted, and it only required about twenty minutes of external heating to complete the reaction. The flask now contained a brownish-yellow liquid from which alcohol was removed by distillation in a current of steam. There remained an aqueous solution of sodium chloride and of sodium ethoxyacetate. When cold, the solution was acidified by adding 165 gms. of concentrated hydrochloric acid which resulted in sodium chloride being deposited. The latter was next filtered off, and the acid extracted with ether and dried over anhydrous sodium sulphate. After several days the sodium sulphate was removed by filtration, the ether evaporated, and the acid submitted to distillation under diminished pressure.

A yield of 90 grammes of a colourless oil was obtained, which boiled at 103.5 - 105° under 17 mm. pressure (57 per cent of the theory).

(2) Preparation of Ethoxyacetyl Chloride.

The following method of preparation is also according to Sommelet*.

* Bull. Soc. Chim., 1907 (IV), 368.

26 grams of ethoxyacetic acid were mixed with 30 grams of purified thionyl chloride at the ordinary temperature, but as the reaction was feeble the mixture was heated on a water-bath at 40°C. and then at 60°C. until there was no longer any gas evolved. The mixture was distilled, and, after removal of excess thionyl chloride, there was obtained a yield of 26 gms. of acid chloride (b.p. 128°C.) As there was a tendency to decompose at this temperature it was thought advisable to redistil the chloride in vacuo.

(3) Preparation of Menthyl Ester.

Although this ester has been described in patent literature, no rotations are recorded for it and the compound does not seem to have been analysed, it having been examined for its therapeutic properties only.

The ester was prepared by making use of the following method, as described in U.S. Pat. 836914, R. Berendes, Elberfeld. F. Bayer & Co. (slightly modified).

Reaction Mixture:-

menthol . . .	16.5 gms.
pyridine . .	8.4 "
benzene . .	53.0 "
ethoxyacetyl Chloride	13.0 "

The mixture was heated on a water-bath for 3 hours, shaken with dilute hydrochloric acid to extract the pyridine and afterwards with dilute sodium carbonate solution and with water. The benzene solution was then separated from the water and dried over calcium chloride. The benzene was removed and the residue distilled in vacuo.

After being twice fractionated under diminished pressure a third fractionation produced no change in the rotatory power.

Yield:- 9 gms. of ester b.p. 148-150/18 mm.
or b.p. 137½-138/7 mm.

Berendes quotes b.p. 153/20 mm.

0.1064 gm ester gave 0.2707 gm CO_2 and .1025 gm H_2O;

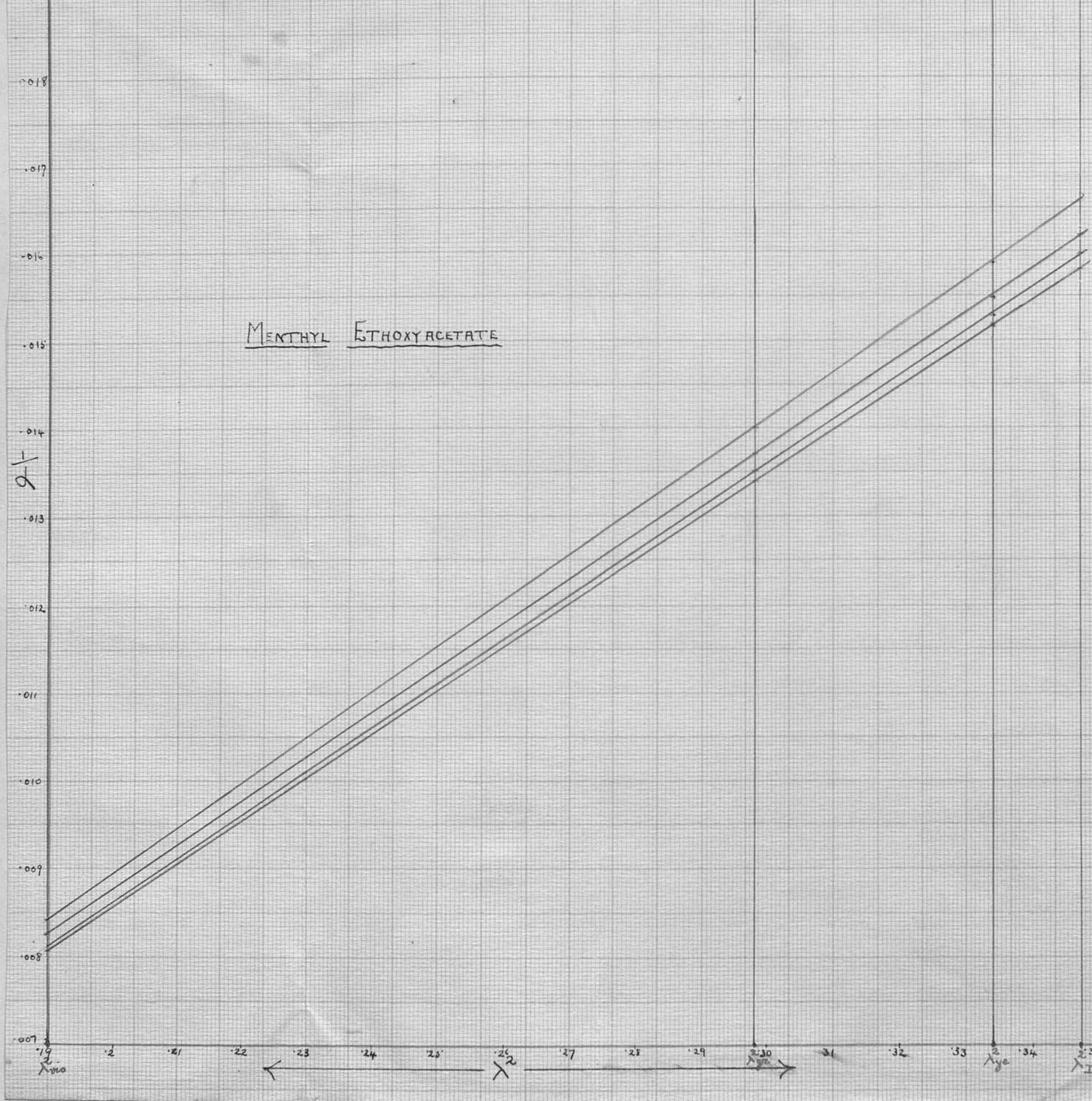
C = 69.38, H = 10.71

$C_{14}H_{26}O_3$ requires C = 69.42, H = 10.74 per cent.

DENSITY DETERMINATIONS.

In the case of this ester density determinations were carried out using a carefully calibrated pyknometer holding about 6 c.c. at room temperature. The densities were calculated with reference to that of water at 4°C.

t°	20	40.6°	58°	79.2°
d_4^t	.9545	.9379	.9242	.9070


MENTHYL ETHOXYACETATE
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λ²
λ²ye
λye
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Temperature.	Length of Observation Tube in mm.	Rotations α	$\frac{\alpha \text{ gr}}{\alpha \text{ D}}$	Drude Equation (one term) K	Drude Equation (one term) λ_0^2	Drude Equation (one term) α(calculated)	Difference. α(obs) - α(calc.)
20.5°	100	α D = 63.31	1.180	20.32	.0262	63.31	± .00
		α ye = 65.96				66.03	- .07
		α gr = 74.68				74.73	- .05
		α vi = 124.18				124.18	± .00
37.0°	50	α D = 31.31	1.182	10.06	.0261	31.31	± .00
		α ye = 32.70				32.64	+ .06
		α gr = 37.01				36.94	+ .07
		α vi = 61.41				61.41	± .00
61.3°	50	α D = 30.89	1.181	9.924	.0261	30.89	± .00
		α ye = 32.28				32.22	+ .06
		α gr = 36.48				36.47	+ .01
		α vi = 60.57				60.57	± .00
93.7°	50	α D = 30.16	1.183	9.663	.0269	30.16	± .00
		α ye = 31.50				31.46	+ .04
		α gr = 35.70				35.63	+ .07
		α vi = 59.31				59.31	± .00

The figures for the different wave-lengths of light at different temperatures can be expressed, within the limits of experimental accuracy, by a Drude equation with one term. Hence the dispersion appears to be simple in character.

MEASUREMENT OF ROTATORY POWERS.

The rotatory powers of this ester were measured in the homogeneous state in a jacketed tube, round which hot water from a thermostat was circulated. The temperature of the liquid was kept constant to within one tenth of a degree for each set of observations.

In the following determinations all rotations are negative.

(Table opposite)

When the above rotations were plotted against the corresponding temperatures, smooth curves were obtained from which the values of the rotatory power at 20°, 40°, 60° and 80° were found to be as follows:-

Temperature	Density.	α_D	α_{ye}	α_{gr}	α_{vi}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[\alpha]_{vi}$
20°	.9545	-31.66	-32.97	-37.36	-62.14	-66.35	-69.10	-78.29	-130.20
40°	.9383	31.25	32.66	36.95	61.30	66.62	69.62	78.76	130.66
60°	.9224	30.85	32.31	36.52	60.59	66.90	70.05	79.18	131.37
80°	.9063	30.44	31.86	36.04	59.84	67.19	70.30	79.54	132.05
90°	.8983	30.23	31.60	35.79	59.46	67.30	70.35	79.69	132.38

PREPARATION OF MENTHYL METHOXYACETATE.

This ester was prepared from monochloracetic acid in the same manner as the ethoxyacetic ester.

(1) $Cl.CH_2COOH \xrightarrow{CH_3ONa} CH_3O.CH_2.COOH.$

(2) $CH_3O.CH_2.COOH \xrightarrow{SOCl_2} CH_3O.CH_2.COCl$

(3) $CH_3O.CH_2.COCl \xrightarrow{Menthol} CH_3O.CH_2.COOC_{10}H_{19}$

(1) Methoxyacetic Acid.

Quantities:- 189 gms. monochloracetic acid.
92 gms. sodium.
928 gms. methyl alcohol.

The method used was exactly similar to that adopted for the preparation of ethoxyacetic acid except that methyl alcohol was used instead of ethyl alcohol. On repeated distillation a liquid b.p. 100.5°/16 mm. was obtained, which solidified in the condenser.

(2) Methoxyacetyl Chloride.

The method used was similar to that employed for ethoxyacetyl chloride*. From 11.5 gms. of methoxyacetic acid and 15 gms of thionyl chloride a yield/

* See Bull. Soc. Chim. 1907, (IV), 368.

yield of 14.4 gms. of crude acid chloride was obtained.

(3) Menthyl Ester of Methoxyacetic Acid.

This ester was prepared from

14.4 gms. of methoxyacetyl chloride

20.7 gms. of menthol

10.5 gms. of pyridine

67 gms. of benzene

by the same method as was used for the ethoxy derivative. After two fractional distillations a third fractionation produced no change in the rotatory power.

Yield 12 gms. of ester (b.p. 141°/16 mm.)

Bayer & Co.(D.R.P.* 191547) quote b.p. 140°/10 mm.

It does not appear to have been previously observed that the liquid compound becomes solid on long standing. From the above preparation a product of m.p. 18°C. was obtained.

0.1196 gm. ester gave 0.2999 gm. CO_2 and .1125 gm. H_2O; C = 68.38, H = 10.45. $C_{13}H_{24}O_3$ requires C = 68.42, H = 10.52 per cent.

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* Patentschrift des Deutschen Reiches.

DENSITY DETERMINATIONS.

Density determinations were again carried out using a calibrated pyknometer holding about 6 c.c. The densities were calculated with reference to that of water at $4^{\circ}C$.

t°	20	40.3	60°	80°
$d_4^{t^{\circ}}$	1.0136	.9964	.9807	.9638

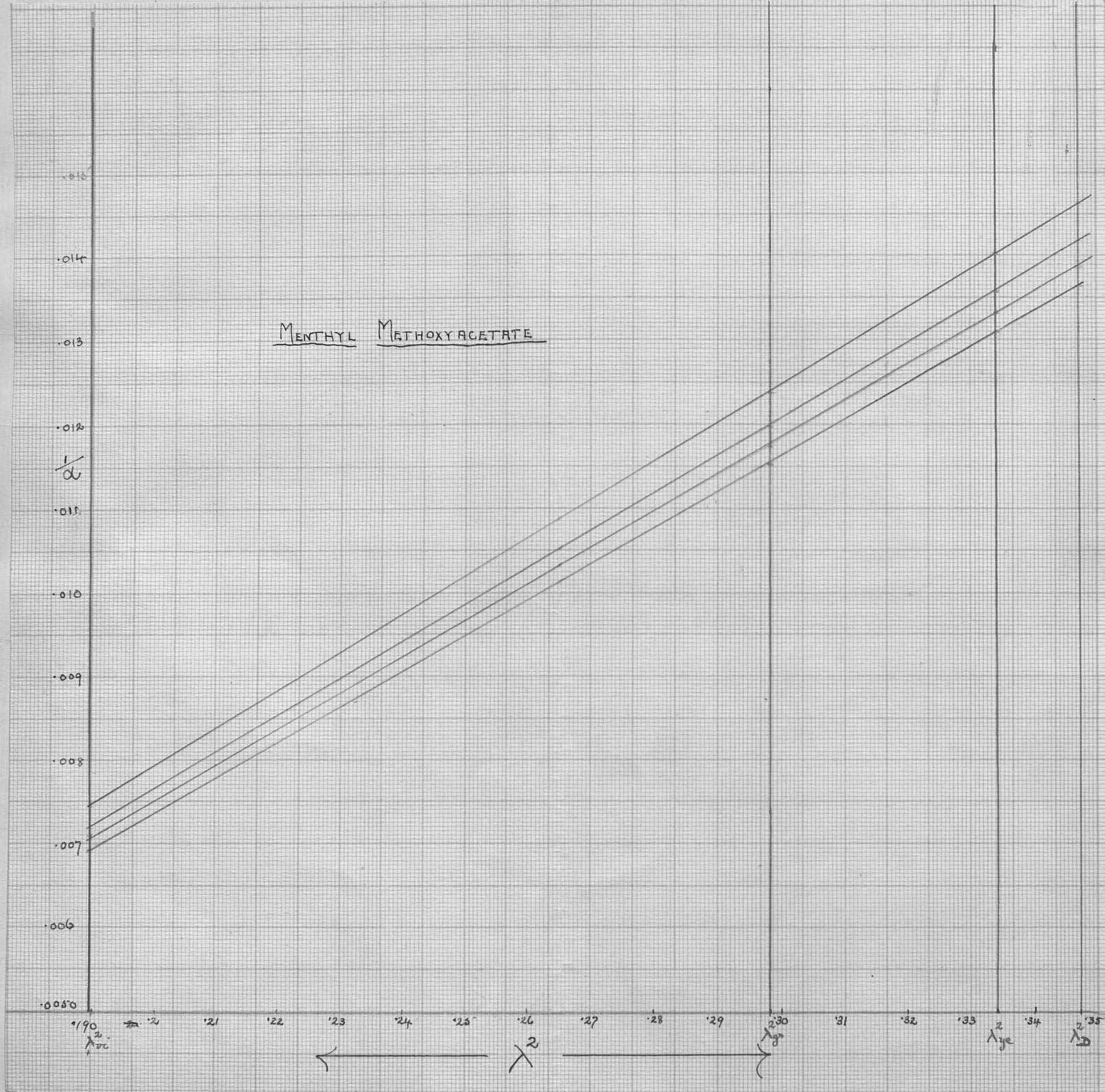
MEASUREMENT OF ROTATORY POWERS.

Except where otherwise stated a 50 mm. jacketed metallic tube was used in the following determinations.

TABLE./

All rotations are negative.

Temperature	Length of Observation Tube in mm.	α (observed)	$\frac{\alpha \text{ gr}}{\alpha \text{ D}}$	Drude Equation (one term) K	Drude Equation (one term) λ_o^2	Drude Equation (one term) α (calculated)	Difference α obs - α calc.
		α_D = 73.33				73.33	± .00
20.5°	100	α_{ye} = 76.47	1.182	23.47	.0273	76.49	- .02
		α_{gr} = 86.70				86.64	+ .06
		α_{vi} = 144.32				144.32	± .00
		α_D = 72.07				72.07	± .00
34.5°	100	α_{ye} = 75.14	1.181	23.03	.0278	75.18	- .04
		α_{gr} = 85.14				85.15	- .01
		α_{vi} = 142.02				142.02	± .00
		α_D = 35.31				35.31	± .00
55.5°	50	α_{ye} = 36.82	1.183	11.26	.0286	36.84	- .02
		α_{gr} = 41.78				41.74	+ .04
		α_{vi} = 69.74				69.74	± .00
		α_D = 34.13				34.13	± .00
93.7°	50	α_{ye} = 35.65	1.183	10.91	.0274	35.61	+ .04
		α_{gr} = 40.40				40.32	+ .08
		α_{vi} = 67.19				67.19	± .00


MENTHYL METHOXYACETATE
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λ²yg
λ²ye
λ²D

The dispersion again appears to be simple in character as the figures for the different wavelengths can be expressed, within the limits of experimental accuracy, by a Drude one-term equation.

The above rotations were plotted against the corresponding temperatures and the values of the rotations at 20°, 40°, 60°, 80° and 90° were read off from the smooth curve.

TABLE./

ROTATORY POWERS AT DIFFERENT TEMPERATURES.

Temp.	Density.	α_D	α_{ye}	α_{gr}	α_{vi}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[\alpha]_{vi}$
20°	1.0136	- 36.67	- 38.26	- 43.36	- 72.16	- 72.35	- 75.49	- 85.56	- 142.39
40°	.9970	35.91	37.35	42.34	70.76	72.04	74.92	84.93	141.95
60°	.9805	35.16	36.66	41.62	69.46	71.72	74.78	84.89	141.68
80°	.9638	34.52	36.06	40.90	68.10	71.63	74.83	84.87	141.32
90°	.9555	34.14	35.77	40.55	67.43	71.47	74.87	84.87	141.14

PREPARATION OF MENTHYL HYDROXYACETATE (MENTHYL ESTER OF GLYCOLLIC ACID).

In the German patent specification D.R.-P, 136411, this compound is described as having been obtained by treating a warm (90°C.) mixture of l-menthol and glycollic acid with hydrochloric acid. No analyses or measurements of rotatory power are quoted.

In the following preparation, dry hydrochloric acid gas was passed for ten minutes in each hour, for a period of fourteen hours, into a mixture of 30 gms. of glycollic acid (3 mols.) and 20 gms. menthol (1 mol.) heated on a steam bath. At the end of this period ether was added to the cooled mass and the ethereal solution was washed successively with water, sodium carbonate solution, and water. After being dried over anhydrous sodium sulphate, the ether was removed, and the residue heated under diminished pressure on an oil bath kept at 130°C. The resulting dark solid was finally crystallised repeatedly from petroleum ether till a 5 per cent solution of the solid in benzene gave a constant rotation figure. The pure ester crystallises in the form of long white needles of melting point 87.5°C. uncorr.

The above specification quotes 87°C.

0.1114 gm ester gave 0.2748 gm CO_2 and 0.1031 gm. H_2O;

C = 67.27, H = 10.28.

$C_{12}H_{22}O_3$ requires C = 67.29, H = 10.28 per cent.

Rotatory Power of l-Menthyl Glycollate in the Homogeneous State.

Temp.	Length of Observation Tube.	Rotations α	$\frac{\alpha gr}{\alpha D}$	Drude Equation (one term) K	Drude Equation (one term) λ_o^2	Drude Equation (one term) α (calculated)	Difference α obs - α calc.	Specific Rotation $[\alpha]$
94.3°	50 mm.	α_D = -36.50				36.50	$\pm$ .00	$[\alpha]_D$ = -77.09
		α_{ye} = -38.09	1.184	11.53	.0312	38.10	- .01	$[\alpha]_{ye}$ = -80.48
		α_{gr} = -43.23				43.21	+ .02	$[\alpha]_{gr}$ = -91.26
		α_{vi} = -72.71				72.71	$\pm$ .00	$[\alpha]_{vi}$ = -153.6

$$D_4^{94.3} = .9469$$

Rotatory Power of l-Menthyl Glycollate in Solvents.

Length of observation tube 20 cms.

Solvent.	Wt. in 100 c.c. Solvent.	Temp.	Rotations α	$\frac{\alpha\ gr}{\alpha\ D}$	Specific Rotations $[\alpha]$
Benzene	5.0040 gms	17.6°	α D = -7.54	1.185	$[\alpha]_D$ =-75.34
			α ye = -7.89		$[\alpha]_{ye}$ =-78.84
			α gr = -8.94		$[\alpha]_{gr}$ =-89.33
			α vi = -14.76		$[\alpha]_{vi}$ =-147.5
Chloroform	5.0032 gms	12.3°	α D = -8.42	1.185	$[\alpha]_D$ =-84.15
			α ye = -8.77		$[\alpha]_{ye}$ =-87.64
			α gr = -9.98		$[\alpha]_{gr}$ =-99.74
			α vi = -16.49		$[\alpha]_{vi}$ =-164.8
	16.1920 gms	"	α D = 27.06		$[\alpha]_D$ = -83.56

Drude One-term Equation Applied to the Above Figures.

Solvent.	Rotations.	Drude Equation (one term) K	λ_o^2	α calc.	Difference α obs - α calc.
Benzene.	α D = -7.54	2.427	.0255	7.54	± .00
	α ye = -7.89			7.86	+ .03
	α gr = -8.94			8.90	+ .04
	α vi = -14.76			14.76	± .00
Chloroform	α D = -8.42	2.646	.0257	8.42	± .00
	α ye = -8.77			8.78	- .01
	α gr = -9.98			9.94	+ .04
	α vi = -16.49			16.49	± .00

Owing to the limits of solubility of this ester in the above solvents having been reached it was not possible to obtain figures for more concentrated solutions.

From the above figures it will be observed that the rotation of l-menthyl glycollate in the fused state at 94.3° ($[\alpha]_D = -77.09°$) approximates very closely to the rotation in 5 per cent solution of benzene ($[\alpha]_D = -75.34$) at 17.6°C. Further, the rotation in chloroform tends to become lower with increasing concentration, thus approaching the value for the fused state.

Since the figures for the different wave-lengths of light can be adequately expressed, within the limits of experimental accuracy, by one term of Drude's equation the dispersion appears to be simple in character.

PREPARATION OF MENTHYL CYANOACETATE.

The preparation of this ester has been fully described by Bowack and Lapworth* but these investigators have only recorded the rotation of the compound in a 2 per cent solution of benzene and for light of one wave length. In order to determine to what extent the rotatory power thus observed was influenced by the presence of the solvent, and to examine the character of the optical dispersion, a quantity of the ester was prepared by the same method.

Menthol (43 gms) and ethyl cyanoacetate (30 gms), mixed in a distilling flask connected with a condenser, were gently heated over an Argand burner at such a temperature that about one drop of alcohol per minute was collected, and the heating was continued until the theoretical amount of liquid had thus been obtained. The product was then submitted to fractional distillation under a pressure of 30 mms. When the temperature of the vapour had risen to about 150°C the distillation was interrupted, and the residue, which partly solidified on cooling, was triturated with alcohol and spread on porous tile. The solid was finally recrystallised from alcohol until the rotation showed no further change.

The/

* Journal of the Chemical Society, 1904, 85, 43.

The purified ester melted sharply at 82.5° (uncor.), Bowack and Lapworth (loc. cit.) quote 83-84°. It was found that in 5 per cent benzene, $[\alpha]_D^{19.2}$ = -79.97°. For the same solvent Bowack and Lapworth quote $[\alpha]_D$ = - 81.15 (2 per cent solution) and Tschugaeff records* $[\alpha]_D$ = - 80.71 (20.55% solution).

* J. Russ. Phys. Chem. Soc. 1902, 34, 606.

In the following determinations all rotations are negative.

ROTATORY POWER OF MENTHYL CYANO-ACETATE.

(1) In Liquid State.

Temp.	Length of Observation Tube.	Rotation α	$\frac{\alpha \text{ gr}}{\alpha \text{ D}}$	Drude Equation (one term) K	Drude Equation (one term) λ_o^2	Drude Equation (one term) α (calculated)	Difference α obs - α calc.	Specific Rotations $[\alpha]$
		α D = 36.71	1.179	11.88	.0238	36.72	- .01	$[\alpha]_D$ = 78.06
		α ye = 38.28				38.29	- .01	$[\alpha]_{ye}$ = 81.39
91.3°	50 mm.	α gr.= 43.28				43.30	- .02	$[\alpha]_{gr.}$ = 92.03
		α vi (not determined owing to slight yellow colour of liquid).						

$$D_4^{91.3} = .9406.$$

(2) In Solvents.

Length of observation tube 2 dcm.

Solvent	Wt. in 100 c.c. of Solvent.	Temp.	Rotations.	$\frac{\alpha\ gr}{\alpha\ D}$	Specific Rotations $[\alpha]$
Benzene	5.0020 gms	19.2°	α D = 8.00 α ye = 8.38 α gr = 9.45 α vi = 15.40	1.181	$[\alpha]_D$ = 79.97 $[\alpha]_{ye}$ = 83.77 $[\alpha]_{gr}$ = 94.46 $[\alpha]_{vi}$ = 153.94
"	11.365 gms	17°C	α D = 4.51 (for $\frac{1}{2}$ decim. tube)	-	$[\alpha]_D$ = 79.37
Chloroform	5.0040 gms	21.8°	α D = 8.39 α ye = 8.81 α gr = 9.96 α vi = 16.83	1.187	$[\alpha]_D$ = 83.83 $[\alpha]_{ye}$ = 88.03 $[\alpha]_{gr}$ = 99.52 $[\alpha]_{vi}$ = 168.17
"	14.9810 gms	21.0°	D = 6.21 (for 50 mm. tube)	-	$[\alpha]_D$ = 82.91

The Drude Equation applied to Rotations in Benzene and Chloroform Solution.

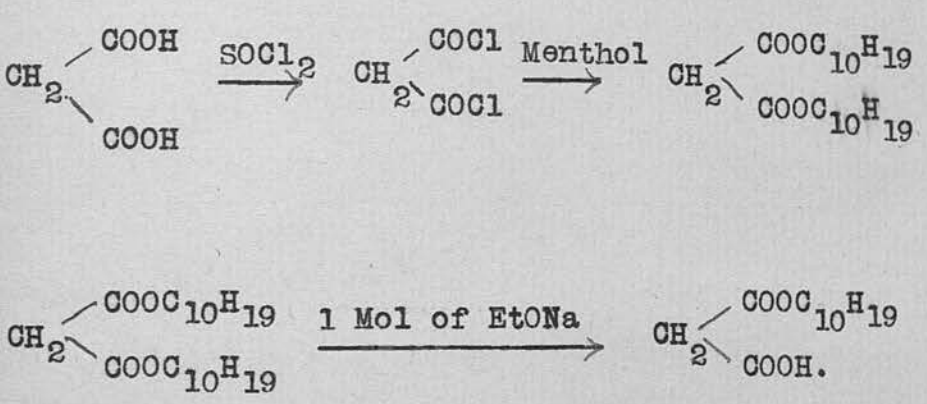
Solvent	Rotations α	Drude equation (one term) K	λ_o^2	α(calculated)	Difference α(obs)-α(calc)
Benzene	α D = 8.00			8.00	± .00
	α ye = 8.38	2.620	.0198	8.34	+ .04
	α gr = 9.45			9.42	+ .03
	α vi = 15.40			15.40	± .00
Chloroform	α D = 8.39			8.38	+ .01
	α ye = 8.81	2.634	.0334	8.76	+ .05
	α gr = 9.96			9.95	+ .01
	α vi = 16.83			16.84	- .01

From the above figures it will be seen that the rotation of menthyl cyanoacetate in the fused state at 91.3° ($[\alpha]_D = -78.06^\circ$), approximates very closely to the rotation in 5 per cent solution in benzene ($[\alpha]_D = -79.97^\circ$) and chloroform ($[\alpha]_D = -83.83^\circ$) at room temperatures. Further, the rotation in benzene and chloroform tends to become lower with increasing concentration, thus approaching the value for the fused state.

The figures for the different wave-lengths of light can be expressed, within the limits of experimental accuracy, by a Drude one-term equation. Hence the dispersion appears to be simple in character.

PREPARATION OF MENTHYL HYDROGEN MALONATE.

Outline of procedure.



Preparation of Dimenthyl Malonate.

Dimenthyl malonate was prepared by a modification of the method of Hilditch*.

A mixture of 50 gms. of malonic acid and 160 gms. of thionyl chloride was heated for two days at 40°C. and then for six hours at 60°C. After removing the excess of thionyl chloride under diminished pressure 62 gms. of impure acid chloride were left behind in the flask.

A mixture of 12.4 gms. of crude acid chloride (about 1 mol) and 27.4 gms. of menthol (a little over 1 mol) was heated on a steam bath for six hours. It/

* J.C.S., 1909, 95, 1571.

It was found that the addition of 14 gms. of pyridine to the above mixture of acid chloride and menthol gave a very much purer product and in greatly increased yield. After cooling, the mass was dissolved in ether, shaken with dilute hydrochloric acid to extract pyridine, and afterwards washed with dilute sodium carbonate solution and with water. The ethereal extract was then distilled in steam to remove excess of menthol, it having been shown by Hall* that dimenthyl malonate was unaffected by such treatment. The non-volatile residue was extracted with ether, dried over calcium chloride and crystallised from methyl alcohol until the rotation was constant.

Yield of pure dimenthyl malonate (m.p. 61.5°) 15 gms., representing 45 per cent of the theory. Rotation in 2-dcm. tube αgr^{20} = -9.36 (in 4.98 per cent solution in chloroform). Hall (loc. cit.) quotes m.p. 61-62°, and rotation in 2-dcm. tube αgr = -9.32 (in 4.98 per cent solution in chloroform).

In the preparation of menthyl hydrogen malonate, 22 gms. of dimenthyl malonate were dissolved in 1 litre of alcohol (96%) and the requisite quantity of sodium in the form of sodium ethoxide was gradually added, the temperature of the liquid being kept at 0°C. After four days the solution was no longer alkaline/

* Journal of the Chemical Society, 1909, 95, 1571.

• ibid., 1923, 123, 109.

alkaline to litmus, and the liquid was then filtered from a small quantity of precipitated disodium malonate. The filtrate was distilled on a water bath under diminished pressure to remove alcohol, and the residue treated with water. The aqueous solution of sodium menthyl malonate so obtained was extracted with ether to remove menthol and evaporated to dryness on a steam bath, when the salt was obtained as a white solid. The sodium menthyl malonate was then dissolved in water, acidified with concentrated hydrochloric acid and the resulting half ester extracted with ether, washed with water and dried over anhydrous sodium sulphate. After the removal of the sodium sulphate and the ether the menthyl hydrogen malonate was crystallised from ethyl acetate until the rotation was constant.

This compound melted at 58.5 - 59° (uncorr.) and had a rotation of $[\alpha]_D^{18.8}$ =-64.10 in 5% benzene solution.

0.1284 gm ester gave 0.3030 gm CO_2 and 0.1048 gm H_2O;

C = 64.36, H = 9.07.

$C_{13}H_{22}O_4$ requires C = 64.46, H = 9.09.

ROTATORY POWER OF MENTHYL HYDROGEN MALONATE.

(1) In Liquid State.

All rotations are negative.

Temp.	Length of Observation Tube.	Rotations α	$\frac{\alpha\ gr}{\alpha\ D}$	Drude Equation (one term) K	Drude Equation (one term) λ_o^2	Drude Equation (one term) α(calculated)	Difference α (obs) - α(calc)	Specific Rotations.
		α D = -33.61	1.184	10.61	.0316	33.61	± .00	$[\alpha]_D$ = -65.65
		α ye = -35.07				35.07	± .00	$[\alpha]_{ye}$ = -68.51
59.5°	50 mm.	α gr = -39.80				39.79	+ .01	$[\alpha]_{gr}$ = -77.75
		α vi = -67.01				67.01	± .00	$[\alpha]_{vi}$ = -130.90
		α D = -32.60	1.184	10.315	.0309	32.59	+ .01	$[\alpha]_D$ = 65.14
		α ye = -33.96				34.01	- .05	$[\alpha]_{ye}$ = 67.86
90.5°	50 mm.	α gr = -38.59				38.59	± .00	$[\alpha]_{gr}$ = 77.11
		α vi = -64.86				64.86	± .00	$[\alpha]_{vi}$ = -129.61

Density of Ester at 59.5°C = 1.0238.

Density of Ester at 90.5°C = 1.0008.

(2) In Benzene Solvent.

Wt. of Ester in 100 ccs. Solvent	Temp.	Length of Observation Tube.	Rotations α	$\frac{\alpha \text{ gr}}{\alpha \text{ D}}$	Specific Rotations. $[\alpha]$
4.914	18.8°C	200 mm.	αD = 6.30	1.185	$[\alpha]_D$=64.10
			αye = 6.56		$[\alpha]_{ye}$=66.74
			αgr = 7.47		$[\alpha]_{gr}$=76.00
			αvi = 12.41		$[\alpha]_{vi}$=126.3
20.078	19°C.	100 mm.	α D = 12.88	-	$[\alpha]_D$=64.14

The Drude Equation Applied to the Above Figures for Benzene Solution.

Rotations α	Drude Equation (one term)			Difference
	K	λ_0^2	α calculated	α (obs) - α (calc.)
αD = 6.30	2.014	.0276	6.30	± .00
αye = 6.56			6.57	- .01
αgr = 7.47			7.44	+ .03
αvi = 12.41			12.41	± .00

The rotation of menthyl hydrogen malonate in benzene tends to become higher with increasing concentration, thus approaching the value for the fused state.

From the above figures it is seen that the dispersion of the compound in the homogeneous state or in benzene solution is normal and apparently simple in character.

PREPARATION OF MENTHYL o- ACETYL-BENZOIC ESTER.

Outline of Method:-

Acetophenone-o-carboxylic acid was first prepared, and was converted into the above menthyl ester by heating it with menthol in the presence of dry hydrochloric acid gas.

Preparation of o-Acetyl-benzoic Acid (acetophenone-o-carboxylic acid). according to Gabriel and Neumann[1].

A mixture of 300 gms. of phthalic anhydride and 400 ccs. of acetic anhydride was heated with 200 gms of freshly fused potassium acetate first on a water-bath, then ten minutes longer on an oil-bath kept at 150-160°C. Hot water was added to the cooled mass and the mixture filtered. The solid was washed with hot water and finally with alcohol till the filtrate was colourless.

Yield of phthalyl acetic acid, 130 gms.

Acetophenone-o-carboxylic acid was prepared directly from phthalyl acetic acid, by heating it with water in a sealed Carius tube for three hours at 200°C.[2]

8 gms. of phthalyl acetic acid gave 3.9 gms. of acetophenone-o-carboxylic acid representing about 57% of the theory.

1 Berichte der Deutschen Chemischen Gesellschaft 1893, 26, 952.

2 Gabriel & Michael, ibid., 1877, 10, 1554.

After several recrystallisations from hot water it melted at 112°C.

Gabriel & Michael quote m.p. 114-115°.

Preparation of Menthyl Ester.

After many unsuccessful attempts to prepare this ester from the acid chloride it was obtained directly from o-acetyl-benzoic acid as follows:-

Dry hydrochloric acid was passed slowly into a mixture of 20 gms. of o-acetyl benzoic acid (1 mol.) and 38 gms. of menthol (2 mols.) which was heated on a steam bath for fourteen hours. The cooled solidified mass was dissolved in ether, washed with water, sodium carbonate, and again with water. After the ethereal solution had been dried over anhydrous sodium sulphate, the ether was removed and the mass heated on an oil-bath to 200°C under 10 mm. pressure, in order to get rid of most of the excess of menthol. The resulting solid was then crystallised repeatedly from petroleum ether. Menthyl o-acetyl-benzoate separated from the above solvent in white needles which melted at 92°C. The pure compound so obtained had no odour.

0.1002 gm ester gave 0.2773 gm CO_2 and 0.0776 gm H_2O;
C = 75.46. H = 8.60. $C_{19}H_{26}O_3$ requires C = 75.49.
H = 8.61 per cent.

DENSITY DETERMINATION.

The density of this ester in the liquid state was determined by use of a calibrated pykometer holding about 1.5 cc.

$$D_4^{94} = 0.9898.$$

ROTATORY POWER OF 1-MENTHYL-o-ACETYLBENZOATE.

(1) In Liquid State.

All rotations are negative.

Temp.	Length of Observation Tube.	Rotations α	$\frac{\alpha\ gr}{\alpha\ D}$	Drude K	Equation λ_o^2	(one term) α(calculated)	Difference. α obs $-\ \alpha$ calc	Specific Rotations
94.0°	50 mm.	α D = 42.84				42.84	± .00	$[\alpha]_D$ = 86.56
		α ye = 45.04	1.213	11.62	.0760	45.02	+ .02	$[\alpha]_{ye}$ = 91.01
		α gr = 51.98				51.98	± .00	$[\alpha]_{gr}$ =105.03
		α vi (Not determined owing to slight yellow colour of liquid).						

$$\left[M\right]_D^{94} = 261.4$$

(2) In Solvents.

Solvent.	Wt of Ester in 100 cc. of Solvent.	Temp.	Length of Observation Tube	Rotations α	$\frac{\alpha\ gr}{\alpha\ D}$	Specific Rotations.
Benzene	5.0000 gms.	20	2 dcm.	α D = 9.42 α ye = 9.90 α gr = 11.46 α vi = 22.03	1.216	$[\alpha]_D$ = 94.2 $[\alpha]_{ye}$ = 99.0 $[\alpha]_{gr}$ = 114.6 $[\alpha]_{vi}$ = 220.3
"	10.0000 gms.	20.5	2 dcm.	α D = 18.85		$[\alpha]_D$ = 94.25
"	20.0104 gms.	20.1	2 dcm.	α D = 37.68 α gr = 45.60	1.211	$[\alpha]_D$ = 94.15 $[\alpha]_{gr}$ = 113.9
Acetone.	5.0128 gms.	20.2	2 dcm.	α D = 8.41 α gr = 10.20	1.213	$[\alpha]_D$ = 83.88 $[\alpha]_{gr}$ = 101.74
Alcohol.	5.0144 gms. 2.0008 gms.	20 19.5	2 dcm.	α D = 8.83 α D = 3.54		$[\alpha]_D$ = 88.04 $[\alpha]_D$ = 88.46

(The more concentrated solutions represent the limit of solubility.)

DRUDE EQUATION APPLIED TO ABOVE ROTATIONS IN BENZENE.

Rotations α	Drude Equation (one term)			Difference.
	K	λ_o^2	α (calculated)	αobs - αcalc.
αD = 9.42			9.42	$\pm$ .00
αye = 9.90	2.59	.0723	9.90	$\pm$ .00
αgr = 11.46			11.47	- .01
αvi = 22.03			22.03	$\pm$ .00

From these figures it is seen that the dispersion of the compound in the homogeneous state or in benzene solution is normal and apparently simple in character.

The rotation of this ester in alcohol tends to become lower with increasing concentration, thus approaching the value for the fused state.

DISCUSSION OF RESULTS.

Before proceeding to discuss the influence of a substituent on the rotatory power of the l-menthyl esters of mono-substituted acetic acids, it is important to know the character of the optical dispersion of these compounds.

The figures quoted in the tables on pp. 11a, 17, 21, 26, 32, show that the observed rotations of the five esters of this type under examination can be satisfied within the limits of experimental error by a Drude equation of one-term. Moreover, the deviations from the calculated values are casual and not systematic. Over the range of temperatures and wave-lengths quoted it can therefore be concluded that the optical dispersion of each of these compounds is normal, and apparently simple in character. This holds true not only for the methoxy, ethoxy, and hydroxy compounds, but also for the cyano and carboxy derivatives, which contain substituents with unsaturated groupings. Menthyl acetate ($[M]_D^{20} = -157.2^\circ$) has been shown to have normal and simple dispersion at low temperatures by Kenyon and Pickard*, and in all probability the dispersion of other menthyl esters of simple substituted/

* J.C.S. 1915, 107, 42.

substituted acetic acids is also of similar nature.

The remaining points of interest will be discussed separately under

(1) Drude constants and dispersion.

(2) Influence of temperature.

(3) Influence of substituents.

(4) Menthyl o-acetyl-benzoate.

TABLE./

DRUDE CONSTANTS AND DISPERSION.

(1) In Homogeneous State.

Substituent Groups.	COOH		OC_2H_5				OCH_3				OH	CN
Temperature	59.5	90.5	20.5	37	61.3	93.7	20.5	34.5	55.5	93.7	94.3	91.3
K	10.61	10.31	10.16	10.06	9.924	9.663	11.73	11.51	11.26	10.91	11.53	11.88
λ_o^2	.0316	.0309	.0262	.0261	.0261	.0269	.0273	.0278	.0286	.0274	.0312	.0238
$\alpha gr / \alpha D.$	1.184	1.184	1.180	1.182	1.181	1.183	1.182	1.181	1.183	1.183	1.184	1.179

Referring to the three compounds for which values have been found for more than one temperature, it will be observed that in each case the value of the rotation constant K decreases with rise of temperature.

From the above values of K in the neighbourhood of 90°, it is evident that K reaches a minimum as a result of the influence of the ethoxy group, which occupies a position very close to hydrogen in the "general polar series".

The dispersion ratio $\alpha gr / \alpha D$ does not vary by more than five in the fourth significant figure for all compounds considered in the liquid state at the above temperatures.

(2) In Solution.

Substituent Group.	COOH	OH		CN.	
Solvent	5% Benzene	5% Benzene	5% Chloroform	5% Benzene	5% Chloroform.
Temperature	18.6	17.6	12.3	19.2	21.6°
K	2.014	2.427	2.646	2.62	2.634
λ_o^2	.0276	.0255	.0257	.0198	.0334
α_{gr} / α_D	1.185	1.185	1.185	1.181	1.187

A similar agreement is found in the dispersion ratio in solutions, for which the greatest difference is six in the fourth significant figure.

In contrast to this regularity we find that the dispersion ratio of menthyl o-acetyl-benzoate is 1.21, both in the liquid state and in solution (see p.37&38).

INFLUENCE OF TEMPERATURE ON MOLECULAR ROTATION.

Substituent Group.	Temperature	Molecular Rotations. Liquid state	In solvents.
- COOH	18.8	-	155.1 (Benzene)
	59.5	158.8	
	90.5	157.6	
$-OC_2H_5$	20°	160.6	
	40	161.2	
	60	161.9	
	80	162.6	
	90	162.8	
$-OCH_3$	20°	165.0	
	40	164.2	
	60	163.5	
	80	163.3	
	90	162.9	
- OH	12.3	-	180.1 (Chloroform)
	17.6	-	161.2 (Benzene)
	94.3	165.0	
-CN	19.2	-	178.3 (Benzene)
	21.8	-	186.9 (Chloroform)
	91.3	174.1	

From above table it is evident that the molecular rotations vary little with change of temperature, a change/

change of sixty degrees centigrade corresponding to an alteration of about two degrees in the molecular rotation.

A curious difference is shown by the ethoxy- and methoxy- derivatives. The rotation of the former rises slightly with increase in temperature, whereas that of the latter falls, thus tending to bring the values together at higher temperatures.

INFLUENCE OF SUBSTITUENTS.

If the molecular rotations of the five l-menthyl esters of substituted acetic acids are considered at a temperature of about 90°, the influence of the groups is found to be in the order

$$CN > OH > OCH_3 > OC_2H_5 > COOH > H.$$

This is in close agreement with the influence of the same substituent groups on a number of other properties of organic compounds. For example, it has been pointed out by Rule (J.C.S. 1924, 125, 2159) that these groups appear to affect the molecular inductive capacity of ethane and benzene in the relative order

$$CN > OH > (OCH_3, OC_2H_5) > COOH > H.$$

The influence of the substituents on the acidic strength of acetic acid is given by

$$CN > COOH > OCH_3 > OC_2H_5 > OH > H.$$

Here the carboxyl and hydroxyl groups have exchanged positions as compared with the other series.

In these esters there is no sign of the positive groups (-CN, -COOH) influencing the rotation in the opposite direction to the negative groups, as is the case with the menthyl esters of substituted benzoic acids and certain derivatives of amyl alcohol (Rule, loc. cit.)

MENTHYL o-ACETYL-BENZOATE.

Temperature	α gr/αD	Molecular Rotations in Liquid State.	Solvents.
20	1.216		284.5 (Benzene 5%)
20.1	1.211		284.3 (Benzene 20%)
20.2	1.213		253.3 (Acetone 5%)
19.5	-		267.0 (Alcohol 2%)
20	-		265.9 (Alcohol 5%)
94°	1.213	261.4	

The rotation of the menthyl ester of o-acetyl-benzoic acid (p. 37) is well above the value for the unsubstituted benzoic ester. Here, therefore, the/

the positive groups CH_3CO- , COOH-, and $-NO_2$ all raise the rotation of menthyl benzoate when introduced into the o- position, whereas the negative substituents, CH_3O-, halogens, and CH_3 depress the value.

Owing to the high melting point (92°) of this ester, the rotations could not be determined in the homogeneous state at a much lower temperature than $94^\circ C$. The influence of solvents on the molecular rotation was noted at 20° (approx.), the more concentrated solutions quoted above representing for each solvent as high a concentration as it was convenient to work with. It will be seen that benzene increases the rotation of the ester as compared with the values obtained for the liquid state, and for alcohol and acetone solutions.

Despite the small differences in rotatory power, the dispersion ratio $\alpha gr/\alpha D$ remains very constant.

C O N C L U S I O N.

If the rotatory powers of the five menthyl esters of substituted acetic acids just described are compared with the values quoted in the literature for other esters derived from acetic acid (see also Rule, loc. cit.), we obtain the following:-

Substituent.	$[M]_D$	Temperature.
H	157	Room
COOH	158.8	59.5°
	157.6	90.5
C_2H_5	159.5	Room
CH_3	160.2	"
OC_2H_5	160.6	"
	162.8	90°
OCH_3	165.0	Room
	162.9	90°
OH	165.0	94.3°
Br	169	Room
Cl	171	"
CN	174.1	91.3°

The relative effect of the groups in these compounds corresponds very closely with the "general polar series". For example, the influence of the above substituents on molecular inductive capacity, as/

as calculated by Rule, is represented by the sequence:

$CN > OH > Cl > Br > (O\ Me, OEt) > (COOH = CH_3) > H$,

in which the position of the carboxyl group is somewhat doubtful. It will be seen that the agreement with optical activity is broken only by a slight displacement of the hydroxyl group.

The influence of the same groups on the acidity of acetic acid is given by

$CN > COOH > Cl > Br > O\ Me > OH > H > CH_3$.

In this case the carboxyl and hydroxyl groups have interchanged positions as compared with the sequence obtained from rotatory power. The methyl group has also undergone a minor displacement.

A connection between the influence of substituents on acidity and on the optical rotation of certain derivatives of active bases has previously been established by Betti (see p. 3.).

The experimental results contained in this thesis also indicate that the regularities observed in the optical activity of the above compounds go hand in hand with a dispersion ratio of constant magnitude.

On the other hand it has been concluded by Rule, chiefly from a consideration of certain amyl derivatives and menthyl esters of benzoic acids, that positive and negative groups may influence rotation in/

in opposite directions and in the order of their true polarity as deduced from the views of Thomson.

From this standpoint the position of the acetyl group can be determined from the molecular inductive capacities of the compounds $CH_3CO.X$. The figures relating to dielectric constants and densities in the following table are taken from Landolt-Börnstein, Physikalisch-chemische Tabellen, and molecular values of inductive capacities are calculated from the formula K M / d.

Series.		Dielectric Const. K.	d	Molec. induc. Capac.
H X	Acetaldehyde	18.5	.80	10.1
Et X	Menthylethyl ketone	17.8	.809	15.8
C_6H_5X.	Acetophenone	18.1	1.03	21

When these values are compared with those of Rule and Paterson (loc. cit.) it is found that the positive groups fall into the order

H X. — , CN, COOH, $COCH_3$, H

Et X. NO_2, CN $COCH_3$, COOH, H

C_6H_5X. NO_2, CN, $COCH_3$ — , H

Again, it has been shown by Camps (cf. Hollemann, Die direkte Einführung von Substituenten, 1910, p. 190) that the nitration of acetophenone at 15° yields a mixture/

mixture of about 55% meta-compound and 45% ortho-compound. Only a trace of p- compound was observed. Comparing these figures with those quoted by Rule and Paterson we obtain

	NO_2	COOH	$COCH_3$
m- compound	93	76	55 per cent

It appears therefore that in the "true polar series" the acetyl group lies in the neighbourhood of the carboxyl group and probably between the latter and hydrogen. Rule places the groups in the order $NO_2 > CH_3CO > COOH > H$, the position of - COOH being determined from the molecular inductive capacities of acetic and propionic acids. The above figures relating to the nitration of acetophenone, together with the high inductive capacity of formic acid, point on the whole to the carboxyl group lying between the nitro and acetyl groups. The series is therefore as follows

F, Cl, Br, I, CH_3, H, $COCH_3$ COOH, NO_2

Hence it might be anticipated that the rotatory power of menthyl o-acetyl-benzoate would lie above that of menthyl benzoate but below that of menthyl hydrogen phthalate. This has now been proved to be the case.

In the following table will be found the molecular rotations and dispersion ratio of menthyl o-acetyl-benzoate/

o-acetyl-benzoate (see p. 37) together with the values for the rotations of other corresponding esters (Cohen) and as many of the dispersion ratios as were determined by Pickard and Kenyon (loc. cit.).

o-Substituent	$[M]_D$	$\alpha gr / \alpha D$
Cl, F	- 194	1.18
Br, I	- 237	1.19
H	- 239	1.18
$COCH_3$	- 261	1.21 (at 94°)
COOH	- 332	1.21 (in solution)
NO_2	- 381	1.26 (at 60°)

In this case it will be seen that the high values associated with the presence of positive groups are accompanied by high values of the dispersion ratios.

It may therefore be concluded that the two types of group effect which have been previously observed, namely, the "general polar effect" visible in molecular inductive capacity, acidic strength and chemical reactivity, and the "true polar effect" as deduced from the electronic theory and traceable in benzene substitution and electromagnetic rotation, are both to be found in optical activity.

The/

The writer wishes to acknowledge his indebtedness to Dr H.G. Rule for his helpful suggestions and advice during the course of the work.
